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Cyclic TPR/TPO experiments for studying Cu/ZnO/Al₂O₃ catalysts using in situ XRD and XAS

P. Kurr^a, M. Behrens^a, A. Trunschke^a, R. Schlögl^a, and T. Ressler^b

^a *Department of Inorganic Chemistry, Fritz-Haber-Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany*

^b *Department of Chemistry, TU Berlin, Secr. C-2, Straße des 17. Juni 135, 10623 Berlin, Germany*

Introduction

Cu/ZnO/Al₂O₃ catalysts are industrial relevant and well established in various commercial reactions, i.e. water-gas-shift and methanol synthesis. Since the interaction of metals with the support is known to affect not only particle morphologies but also the catalytic properties, the active copper phase has to be supported in an appropriate manner to obtain an optimal dispersion in the Cu/ZnO/Al₂O₃ catalyst without allowing segregation. Thus, the combination of temperature programmed reduction/ oxidation (TPR/ TPO) with in situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) is a useful technique for studying the role of metal support interactions in Cu/ZnO/Al₂O₃ catalysts.

Experimental

Repeated reduction and subsequent oxidation experiments were performed with a Cu/ZnO/Al₂O₃ catalyst prepared by co-precipitation. For that purpose, temperature programmed reduction was carried out in a flow of 5 vol.% H₂/Ar at 573 K with a heating rate of 2 Kmin⁻¹. After cooling to RT a 5 vol.% O₂/He mixture was used as an oxidant during temperature programmed oxidation. Each oxidation of the activated Cu/ZnO/Al₂O₃ catalyst was performed at 603 K with a heating rate of 2 Kmin⁻¹.

Results and discussion

Figure 1a shows the TPR profiles after repeated reduction and subsequent oxidation cycles of a Cu/ZnO/Al₂O₃ catalyst. Generally, the temperature at which reduction of

the Cu/ZnO/Al₂O₃ catalyst occurs is higher for the 1st reduction than that for the subsequent cycles. Accordingly, a downshift in maxima of reduction temperature of about 4 K has been identified between the 1st and the 2nd reduction cycle which is, in addition, accompanied by a considerable change of the shape of the reduction profile. Further subsequent oxidation and re-reduction revealed only marginal differences with respect to reduction/ oxidation temperature, peak profile shape and consumed hydrogen/ oxygen compared to the fresh sample (Fig. 1a).

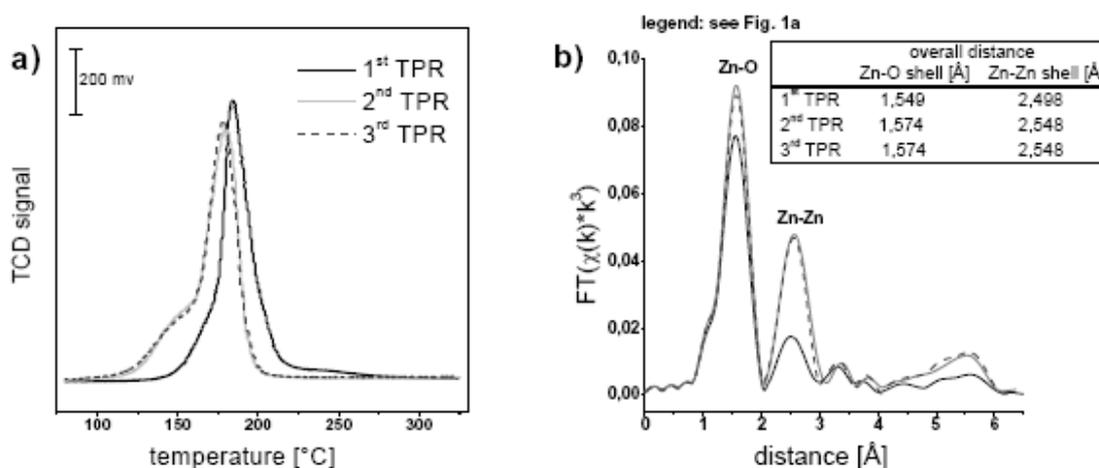


Figure 1: H₂ consumption during cyclic TPR treatments (a) and Zn K- edge EXAFS recorded after TPR cycles at ambient temperature (b).

Apparently, irreversible structural changes of Cu in the Cu/ZnO/Al₂O₃ catalyst occurred during the first TPR/ O cycle. In situ XRD and Cu K- edge EXAFS revealed a steady increase in Cu crystallite size from 3.8 to 5.0 to 6.0 nm after the individual reduction cycles. However, the increase in Cu crystallite size had no direct impact on the reduction temperature of the Cu component. Conversely, a transformation of an initially narrow Cu particle size distribution found for the fresh sample to a pronounced bimodal distribution is reflected in the shape of the TPR profiles (Fig. 1a). Moreover, ZnO in the Cu/ZnO/Al₂O₃ catalyst also exhibited an irreversible change in the microstructure which coincides well with the observed downshift in temperature. After reduction of the fresh sample the microstructure of ZnO as well as the redox behavior of Cu remain almost unchanged (Figs. 1a-b). Thus, the observed reduction characteristics of Cu are strongly affected by an irreversible loss of metal support interaction in the Cu/ZnO/Al₂O₃ catalyst during the TPR/ O treatments.